

(19)



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(11)

**EP 0 848 250 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
17.06.1998 Bulletin 1998/25

(51) Int Cl.<sup>6</sup>: G01N 27/407, F01N 7/00

(21) Application number: 97309954.2

(22) Date of filing: 10.12.1997

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

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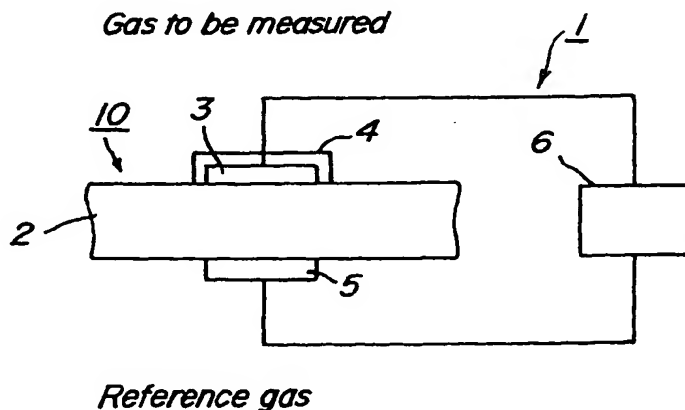
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**(54) Gas sensor and method for diagnosing malfunction of exhaust gas purifying apparatus**

(57) In a gas sensor for measuring a specific gas component especially hydrocarbon in a gas to be measured, a hydrocarbon prevention filter (4) preferably made of zeolite is used. There is obtained the oxygen concentration difference between (i) the oxygen concentration in the gas being measured from which hydrocarbons are removed by the hydrocarbon prevention fil-

ter and further combustible components are removed, measured by a cell (2,3,5), and (ii) a known oxygen concentration or an oxygen concentration in the gas from which only the combustible components are removed. The oxygen amount necessary for a combustion of hydrocarbons is then calculated to provide the hydrocarbon concentration in the gas to be measured.

**FIG. 1**



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## Description

Background of the Invention5 Field of the Invention

The present invention relates to a gas sensor used for measuring a concentration of a specific gas component especially hydrocarbon in an exhaust gas generated from for example automobiles, a method of measuring a gas component by utilizing such a gas sensor, and a method of diagnosing a malfunction of an exhaust gas purifying apparatus.

Related Art Statement

Recently, there is a requirement such that a malfunction of an exhaust gas purifying apparatus provided at a downstream position of an automobile engine is detected and such a malfunction is informed for a driver. This kind of malfunction can be detected by measuring an increase of hydrocarbon concentration in an exhaust gas which is passed through the exhaust gas purifying apparatus. In order to limit such an increase of hydrocarbon concentration, there is OBDII in California State of USA in which a total amount of NMHC (non methane hydrocarbon) is limited under a predetermined level. Therefore, there is a necessity for measuring a concentration of hydrocarbon in the exhaust gas of automobiles.

Usually, as a gas sensor for measuring a concentration of hydrocarbon in a gas to be measured, a total hydrocarbon analyzer utilizing a hydrogen flame ionization method is known. This total hydrocarbon analyzer measures a hydrocarbon concentration by supplying hydrocarbons into a hydrogen flame to perform a ionization, measuring such an ionization as a small ion current by applying DC voltage between electrodes which sandwich the hydrogen flame, and calculating the hydrogen concentration from the thus measured small ion current.

In the total hydrocarbon analyzer for measuring an HC (hydrocarbon) concentration mentioned above, it is possible to measure accurately the HC concentration in the exhaust gas. However, in the total hydrocarbon analyzer utilizing a hydrogen flame ionization method, it is necessary to use a hydrogen flame. Also it is necessary to use a large and complicated mechanism. As a result, there is a problem such that it is not possible to construct a compact sensor which can be used in automobiles by the total hydrocarbon analyzer.

Summary of the Invention

An object of the invention is to eliminate or reduce these drawbacks and to provide a gas sensor which can perform an accurate concentration measurement even if a size is compact, a method of measuring a gas component by utilizing such a gas sensor, and a method of diagnosing a malfunction of an exhaust gas purifying apparatus by utilizing such a gas sensor.

According to a first aspect of a gas sensor of the invention, a gas sensor for measuring a hydrocarbon concentration in a gas to be measured, comprises: a sensor portion which includes a hydrocarbon prevention filter for preventing a pass of hydrocarbons; a combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter; and an oxygen measurement means for measuring an oxygen concentration of a gas to be measured from which said combustible components are removed by said combustion catalyst.

According to a first aspect of a method of measuring a gas component of the invention, a method of measuring a hydrocarbon concentration in a gas to be measured by utilizing the first aspect of the gas sensor according to the invention, comprises the steps of: measuring an oxygen concentration in a gas to be measured, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said combustion catalyst, by said oxygen measurement means; calculating an oxygen concentration difference between said oxygen concentration measured in a gas to be measured, from which only combustible components are removed; and calculating a hydrocarbon concentration in a gas to be measured on the basis of the thus obtained oxygen concentration difference.

According to a second aspect of the gas sensor of the invention, a gas sensor for measuring a hydrocarbon concentration in a gas to be measured, comprises: a first sensor portion including a hydrocarbon prevention filter for preventing a pass of hydrocarbons, a first combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter, and a first oxygen measurement means for measuring a first oxygen concentration in a gas to be measured from which said combustible components are removed by said first combustion catalyst; a second sensor portion including a second combustion catalyst for removing combustible components in a gas to be measured, and a second oxygen measurement means for measuring a second

oxygen concentration in a gas to be measured from which said combustible components are removed by said second combustion catalyst; and a process means for calculating an oxygen concentration difference between said first oxygen concentration measured by said first oxygen measurement means and said second oxygen concentration measured by said second oxygen measurement means and then calculating a hydrocarbon concentration in a gas to be measured on the basis of the thus calculated oxygen concentration difference.

According to a second aspect of a method of measuring a gas component of the invention, a method of measuring a hydrocarbon concentration in a gas to be measured by utilizing the first aspect of the gas sensor according to the invention, comprises the steps of: measuring a first oxygen concentration in a gas to be measured, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said first combustion catalyst, by said first oxygen measurement means; measuring a second oxygen concentration in a gas to be measured, from which combustible components are removed by said second combustion catalyst, by said second oxygen measurement means; calculating an oxygen concentration difference between said first oxygen concentration measured by said first oxygen measurement means and said second oxygen concentration measured by said second oxygen measurement means; and calculating a hydrocarbon concentration in a gas to be measured on the basis of the thus calculated oxygen concentration difference.

According to a third aspect of a gas sensor for diagnosing a malfunction of an exhaust gas purifying apparatus in automobiles, comprises: a sensor including a hydrocarbon prevention filter for preventing a pass of hydrocarbons, a combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter, and an oxygen measurement means for measuring an oxygen concentration of a gas to be measured from which said combustible components are removed by said combustion catalyst; and an indication means for indicating a malfunction of said exhaust gas purifying apparatus for a driver, when an oxygen concentration difference between said oxygen concentration in a gas measured by said oxygen measurement means and an oxygen concentration in a gas measured by an oxygen sensor for controlling an air/fuel ratio in an engine reaches to an oxygen concentration equivalent to a predetermined level of hydrocarbons, e.g. a regulatory maximum hydrocarbon level.

According to the invention, a method of diagnosing a malfunction of an exhaust gas purifying apparatus by utilizing the third aspect of the gas sensor according to the invention, comprises the steps of: measuring an oxygen concentration in an exhaust gas passed through said exhaust gas purifying apparatus, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said combustion catalyst, by said oxygen measurement means; calculating an oxygen concentration difference between said oxygen concentration measured by said oxygen measurement means and an oxygen concentration measured by said oxygen sensor for controlling an air/fuel ratio of an engine; and indicating a malfunction of said exhaust gas purifying apparatus for a driver when the thus calculated oxygen concentration difference reaches to an oxygen concentration equivalent to a predetermined, e.g. regulatory maximum, level of hydrocarbons.

In the present invention, the hydrocarbon prevention filter preferably made of zeolite is used. Therefore, if an oxygen concentration difference between an oxygen concentration in a gas to be measured from which hydrocarbons are removed by the hydrocarbon prevention filter and further combustible components are removed and a known oxygen concentration (first aspect of the invention) or an oxygen concentration in a gas from which only combustible components are removed (second aspect of the invention), and an oxygen amount necessary for a combustion of hydrocarbons is calculated, it is possible to measure a hydrocarbon concentration in a gas to be measured on the basis of the thus calculated oxygen amount.

Moreover, in the present invention, if an oxygen concentration difference between an oxygen concentration in an exhaust gas at a downstream of an exhaust gas purifying apparatus from which hydrocarbons are removed by the hydrocarbon prevention filter and further combustible component are removed and an oxygen concentration in an exhaust gas which is not passed through the exhaust gas purifying apparatus, and an oxygen amount necessary for a combustion of hydrocarbons is calculated, it is possible to inform a driver of an indication showing a malfunction of the exhaust gas purifying apparatus preferably by a light ON of a lamp when the thus calculated oxygen amount reaches to an oxygen amount equivalent to a regulation level of hydrocarbons.

#### Brief Description of the Drawing

Fig. 1 is a schematic view showing one embodiment of a gas sensor according to the present invention;  
 Fig. 2 is a schematic view illustrating another embodiment of the gas sensor according to the present invention;  
 Fig. 3 is a schematic view depicting still another embodiment of the gas sensor according to the present invention;  
 Fig. 4 is a schematic view for explaining a method of measuring a hydrocarbon concentration by utilizing the gas sensor shown in Figs. 2 and 3;  
 Fig. 5 is a schematic view showing one step of a gas sensor manufacturing method in the present invention;  
 Fig. 6 is a schematic view illustrating an electrode construction of the gas sensor according to the present invention;  
 Fig. 7 is a schematic view depicting one embodiment of an apparatus which is used for an examination of a hy-

drocarbon measurement in the present invention; and

Fig. 8 is a graph showing a relation between oxygen concentration difference and HC concentration.

### Description of the Preferred Embodiments

Fig. 1 is a schematic view showing one embodiment of a gas sensor according to a first aspect of the invention. In the embodiment shown in Fig. 1, a gas sensor 1 comprises a sensor portion 10 and a process portion 6. The sensor portion 10 comprises an oxygen ion conduction member 2; a measurement electrode 3 arranged on one main plane of the oxygen ion conduction member 2, which is disposed to a gas to be measured; a hydrocarbon prevention filter 4 arranged on the measurement electrode 3 for preventing a pass of hydrocarbons; and a reference electrode 5 arranged on the other main plane of the oxygen ion conduction member 2, which is disposed to a reference gas. In this embodiment, the measurement electrode 5 made of platinum serves as a combustion catalyst. In the process portion 6, an oxygen concentration in a gas, from which hydrocarbons are removed by the hydrocarbon prevention filter 4 and further combustible components are removed by the measurement electrode 5, is measured on the basis of an electromotive force generated between the measurement electrode 3 and the reference electrode 5, and an oxygen concentration difference between the thus measured oxygen concentration and an oxygen concentration measured preliminarily in a gas from which only combustible components are removed, so that a hydrocarbon concentration in a gas to be measured can be obtained on the basis of the thus calculated oxygen concentration difference.

In the embodiment shown in Fig. 1, the gas sensor 1 is constructed by the sensor portion 10 and the process portion 6. However, in the case that the oxygen concentration measured preliminarily in a gas from which combustible components including hydrocarbon are removed is a standard value such as 0, the oxygen concentration measured by the sensor portion 10 shows directly the oxygen concentration difference mentioned above. In this case, the gas sensor 1 according to a first aspect of the invention may be constructed by the sensor portion 10 only.

As the hydrocarbon prevention filter 4, it is preferred to use a zeolite membrane. The zeolite membrane is generally known in this technical field, and a filtering property of the zeolite membrane can be selected by using a hydrothermal synthesis method. Therefore, in this embodiment, the hydrocarbon prevention filter 4 is designed to have a filtering property such that various kinds of hydrocarbon molecules in a gas to be measured are not passed but the other molecules except for the hydrocarbon molecules are passed. Moreover, as the oxygen ion conduction member 2, it is preferred to use zirconia. Further, as the measurement electrode 3 and the reference electrode 4, it is preferred to use a platinum electrode. In this embodiment, the gas sensor 1 having the construction shown in Fig. 1 is used under an atmosphere in which the oxygen concentration after a combustion of the combustible components is previously known. Therefore, it is possible to detect the hydrocarbon concentration from the oxygen concentration difference between the oxygen concentration measured by the sensor portion 10 and the oxygen concentration after the combustion of the combustible components.

Fig. 2 is a schematic view showing one embodiment of a gas sensor according to the second aspect of the invention. In the embodiment shown in Fig. 2, a gas sensor 21 comprises a first gas sensor 11, a second gas sensor 16 and a process portion 20. The first gas sensor 11 comprises an oxygen ion conduction member 12; a measurement electrode 13 arranged on one main plane of the oxygen ion conduction member 12, which is disposed to a gas to be measured; a hydrocarbon prevention filter 14 arranged on the measurement electrode 13 for preventing a pass of hydrocarbons; and a reference electrode 15 arranged on the other main plane of the oxygen ion conduction member 12, which is disposed to a reference gas. Moreover, the second gas sensor 16 having the same construction as the known one comprises an oxygen ion conduction member 17; a measurement electrode 18 arranged on one main plane of the oxygen ion conduction member 17, which is disposed to a gas to be measured; and a reference electrode 19 arranged on the other main plane of the oxygen ion conduction member 17, which is disposed to a reference gas. Further, in the process portion 20, an oxygen concentration difference between the oxygen concentration in a gas measured by the first gas sensor 11 and the oxygen concentration in a gas measured by the second gas sensor 16 is calculated, and a hydrocarbon concentration in a gas to be measured is calculated on the basis of the thus calculated oxygen concentration difference. In the embodiment shown in Fig. 2, the measurement electrode 13 serves as a first combustion catalyst, and the measurement electrode 18 serves as a second combustion catalyst.

As the hydrocarbon prevention filter 14, as is the same as the embodiment shown in Fig. 1, it is preferred to use a zeolite membrane. The zeolite membrane is generally known in this technical field, and a filtering property of the zeolite membrane can be selected by using a hydrothermal synthesis method. Therefore, in this embodiment, the hydrocarbon prevention filter 14 is designed to have a filtering property such that various kinds of hydrocarbon molecules in a gas to be measured are not passed but the other molecules except for the hydrocarbon molecules are passed. Moreover, as the oxygen ion conduction members 12 and 17, it is preferred to use zirconia. Further, as the measurement electrodes 13 and 18 and the reference electrodes 15 and 19, it is preferred to use a platinum electrode.

Fig. 3 is a schematic view showing still another embodiment of a gas sensor according to the invention. In this embodiment, as compared with the embodiment shown in Fig. 2, it is different that the first gas sensor and the second

gas sensor are formed on the same oxygen ion conduction member. That is to say, in the embodiment shown in Fig. 3, a gas sensor 31 comprises an oxygen ion conduction member 33 having a heater 32; a first measurement electrode 34-1 and a second measurement electrode 34-2 arranged on one main plane of the oxygen ion conduction member 33; a hydrocarbon prevention filter 35 arranged on the first measurement electrode 34-1; and a reference electrode 36 arranged on the other main plane of the oxygen ion conduction member 33. In this embodiment, materials used for respective portions are not limited. However, it is preferred to use zirconia as the oxygen ion conduction member 33, a platinum electrode as the first measurement electrode 34-1 and the second measurement electrode 34-2, and a zeolite membrane as the hydrocarbon prevention filter 35.

In the embodiment mentioned above, the first measurement electrode 34-1 and the reference electrode 36 construct a first sensor portion, and the second measurement electrode 34-2 and the reference electrode 36 construct a second sensor portion. Moreover, a numeral 37 shows a process portion in which an oxygen concentration difference between an oxygen concentration in a gas measured by the first sensor portion and an oxygen concentration in a gas measured by the second sensor portion and a hydrocarbon concentration is calculated on the basis of the thus calculated oxygen concentration difference. Moreover, in the embodiment shown in Fig. 3, the first measurement electrode 34-1 serves as a first combustion catalyst and the second measurement electrode 34-2 serves as a second combustion catalyst.

Fig. 4 is a schematic view for explaining a method of measuring a hydrocarbon concentration by utilizing the gas sensor having the construction shown in Figs. 2 and 3. Then, the method of measuring a hydrocarbon concentration will be explained with reference to Fig. 4. At first, a gas to be measured which includes  $O_2$ ,  $CO_2$ ,  $H_2O$ ,  $CO$ ,  $NO_x$ ,  $HC$  and so on is brought into contact with the first measurement electrode 13(34-1) serving also as the first combustion catalyst and the second measurement electrode 18(34-2) serving also as the second combustion catalyst. In this case, since a gas supplying to the first measurement electrode 13(34-1) is passed through the hydrocarbon prevention filter 14(35), hydrocarbons are removed from a gas supplying to the first measurement electrode 13(34-1). Then, when a gas to be measured is brought into contact with the first measurement electrode 13(34-1) and the second measurement electrode 18(34-2), combustible components in a gas to be measured are burnt and removed from a gas to be measured. In this case,  $CO$  component is burnt at the first combustion catalyst 13(34-1), and  $CO$  component and hydrocarbon ( $HC$ ) component are burnt at the second combustion catalyst 18(34-2).

Then, a first oxygen concentration in a gas to be measured, in which combustible components except for  $HC$  component are burnt, is measured by a first oxygen measurement means consisting of the first measurement electrode 13(34-1) and the reference electrode 15(36). In addition, a second oxygen concentration in a gas to be measured, in which combustible components including  $HC$  component are burnt, is measured by a second oxygen measurement means consisting of the second measurement electrode 18(34-2) and the reference electrode 19(36). Then, in the process portions 20(37), an oxygen concentration difference between the first oxygen concentration and the second oxygen concentration is calculated. The thus calculated oxygen concentration difference shows an oxygen amount necessary for burning hydrocarbons ( $HC$ ). Therefore, if a relation between the oxygen amount necessary for burning hydrocarbons and a hydrocarbon amount i.e. a hydrocarbon concentration is preliminarily measured, it is possible to calculate a hydrocarbon concentration from the oxygen concentration difference on the basis of the thus preliminarily measured relation.

In the embodiments mentioned above, the gas sensor is utilized for measuring a hydrocarbon concentration in a gas to be measured. According to the invention, it is further possible to diagnose a malfunction of an exhaust gas purifying apparatus in automobiles by utilizing a gas sensor having the same construction as that of the embodiments mentioned above. In this case, it is assumed that a malfunction of the exhaust gas purifying apparatus is dependent upon an increase of a hydrocarbon concentration in an exhaust gas which passes through the exhaust gas purifying apparatus. Then, a malfunction of the exhaust gas purifying apparatus is informed for a driver by means of an indication preferably a light ON of a lamp, when an oxygen amount equivalent to a regulation level of a hydrocarbon concentration reaches to a predetermined value. That is to say, the gas sensor 1 having a construction shown in Fig. 1 is arranged at a downstream position of the exhaust gas purifying apparatus in automobiles, and an oxygen concentration of the exhaust gas passed through the exhaust gas purifying apparatus is measured by the gas sensor 1. Then, an oxygen concentration difference between the thus measured oxygen concentration and an oxygen concentration in the exhaust gas measured by an oxygen sensor used for controlling an air/fuel ratio in an engine which is arranged at an upstream position of the exhaust gas purifying apparatus but at a downstream position of the engine is calculated, and an oxygen amount necessary for a combustion of hydrocarbons is calculated on the basis of the thus calculated oxygen concentration difference. Then, a malfunction of the exhaust gas purifying apparatus is informed to a driver by for example lighting ON of a lamp. The gas sensor according to the third aspect of the invention mentioned above can be applied for OBDII.

Hereinafter, an actual example will be explained.

Example

## (1) Manufacturing of gas sensor:

A gas sensor having a hydrocarbon prevention filter made of a zeolite membrane was manufactured as follows. At first, as shown in Fig. 5, a base oxygen sensor was manufactured according to a known manufacturing method. This type of gas sensor was referred to TF HEGO (Thick Film Exhaust Gas Oxygen) sensor. Then, alumina was coated on an electrode 1 by a thermal spraying method to provide a porous alumina layer having a thickness of 100  $\mu\text{m}$  the electrode 1 only. Then, a strip paint was arranged on the portion except for the electrode 1 on which the porous alumina layer was provided.

After that, the gas sensor was dipped in a sol solution including a zeolite raw material, and was dried for 5 hours at 90°C. As the sol solution including a zeolite raw material, a colloidal silica was used for Si raw material, aluminum sulfate was used for Al raw material, and sodium hydroxide was used for Na raw material. Moreover, the sol solution was prepared by adjusting  $\text{SiO}_2/\text{Al}_2\text{O}_3$  to 25 and  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  to 0.34 to obtain a water amount of 85%. Then, the strip paint was peeled off to obtain a gas sensor in which only the electrode 1 made of porous alumina layer was coated by a zeolite raw material. Then, an autoclave treatment was performed for the gas sensor.

The autoclave treatment was performed by a hydrothermal treatment for 96 hours at 180°C under the condition such that triethylamine and ethylene diamine were used as a template material. Then, the gas sensor was cooled in the autoclave, and then a boiling wash treatment was performed with respect to the gas sensor picked up from the autoclave by changing a distilled water three times. After the gas sensor was dried up, in order to remove the template material provided in micro holes of zeolite, a calcination was performed for 5 hours at 500°C. A cross section of the electrode 1 manufactured as mentioned above was shown in Fig. 6. In this case, it was confirmed that the thus manufactured zeolite was ZSM-5 by means of XRD.

## (2) Measuring of hydrocarbons by the thus manufactured gas sensor:

An apparatus used for this examination, in which m-xylene was used as a hydrocarbon (HC) to be measured, was shown in Fig. 7. An examination gas was prepared by means of mass-flow controllers to obtain compositions shown in the following Table 1 and Table 2. Then, the thus prepared examination gas was introduced into a measurement chamber in which the gas sensor manufactured according to the above (1) step was arranged. In this case, a bubbling treatment at 0°C was performed with respect to m-xylene by using a nitrogen gas. By utilizing this bubbling treatment, a nitrogen component was introduced into the measurement chamber as a carrier gas. The gas sensor was preliminarily heated at 800°C by a heater provided in the measurement chamber. Then, electromotive forces generated between the electrode 1 and the electrode 3 and between the electrode 2 and the electrode 3 were measured respectively by a voltmeter, and the thus measured electromotive force was converted into an oxygen concentration on the basis of Nemst equation. Moreover, actual hydrocarbon concentration (HC concentration) of the same examination gas was measured by the hydrogen flame type HC analyzer.

Table 1

m-xylene (ppm)	10	50	100	200	500	1000	5000
oxygen (%)	5	5	5	5	5	5	5
carbon dioxide (%)	10	10	10	10	10	10	10
water (%)	10	10	10	10	10	10	10
nitrogen	remainder	remainder	remainder	remainder	remainder	remainder	remainder

Table 2

m-xylene (ppm)	20	200	2000	50	500	1000	5000
oxygen (%)	10	10	10	5	5	5	5
carbon dioxide (%)	10	10	10	20	20	20	20
water (%)	10	10	10	10	10	10	10

Table 2 (continued)

nitrogen	remainder	remainder	remainder	remainder	remainder	remainder	remainder
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The measurement results were shown in Table 3 and Fig. 8 respectively. In Table 3 and Fig. 8. A symbol ● shows a relation between an HC concentration measured by the hydrogen flame type HC analyzer and an oxygen concentration difference measured by the gas sensor according to the invention in the case that a m-xylene concentration is varied in an range of 10-5000 ppm in an examination gas including an oxygen concentration of 5%, an carbon dioxide concentration of 10% and a water of 10%. Moreover, a symbol ▲ and a symbol □ show the same relation in the same examination gas except for an oxygen concentration of 10% (▲) and a carbon dioxide concentration of 20% (□). As clearly understood from Fig. 8, all the cases mentioned above have an excellent linearity between the HC concentration and the oxygen concentration difference. Therefore, it is understood that a m-xylene concentration can be measured on the basis of the oxygen concentration difference measured by the gas sensor according to the invention.

Table 3

HC concentration (ppm)	oxygen concentration difference (ppm)		
	●	▲	□
75	960		
407	4500		
800	10500		
1580	23000		
4015	50087		
8002	102119		
39880	505033		
164		2080	
1589		20500	
15788		201330	
399			4650
3897			48900
8055			102500
40123			495750

In this examination, ZSM-5 membrane was used as the hydrocarbon prevention filter and metaxylene was used as a hydrocarbon to be measured. However, it is possible to measure various kinds of hydrocarbons by suitably selecting a zeolite having a suitable diameter for a hydrocarbon to be measured from A-type zeolite, X-type zeolite, Y-type zeolite, DD3R, DOH, silica soda light and so on. Moreover, in this examination, only metaxylene was used as a hydrocarbon to be measured. However, in the case that more than two kinds of hydrocarbons are mixed to form a mixed gas, if a relation between an oxygen concentration difference according to the invention in the mixed gas and an amount of oxygen necessary for burning the mixed gas is preliminarily obtained, a hydrocarbon concentration of the mixed gas in which more than two kinds of hydrocarbons are mixed can be measured in the same manner as mentioned above.

As clearly understood from the above explanations, according to the invention, the hydrocarbon prevention filter preferably made of zeolite is used. Therefore, if an oxygen concentration difference between an oxygen concentration in a gas to be measured from which hydrocarbons are removed by the hydrocarbon prevention filter and further combustible components are removed and a known oxygen concentration or an oxygen concentration in a gas from which only combustible components are removed, and an oxygen amount necessary for a combustion of hydrocarbons is calculated, it is possible to measure a hydrocarbon concentration in a gas to be measured on the basis of the thus calculated oxygen amount. Moreover, since the gas sensor for measuring a hydrocarbon concentration in a gas to be measured according to the invention can be constructed on the basis of a small oxygen sensor, it is possible to form the gas sensor according to the invention in a compact manner, and thus the gas sensor according to the invention can be installed in automobiles. Further, the gas sensor according to the invention can be utilized for a diagnose of a malfunction of the exhaust gas purifying apparatus in automobiles.



## Claims

1. A gas sensor for measuring a hydrocarbon concentration in a gas to be measured, comprising: a sensor portion which includes a hydrocarbon prevention filter for preventing a pass of hydrocarbons; a combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter; and an oxygen measurement means for measuring an oxygen concentration of a gas to be measured from which said combustible components are removed by said combustion catalyst.
2. The gas sensor according to claim 1, wherein said oxygen measurement means comprises: an oxygen ion conduction member; a measurement electrode arranged on one main plane of said oxygen ion conduction member, which is disposed to a gas to be measured; and a reference electrode arranged on the other main plane of said oxygen ion conduction member, which is disposed to a reference gas; in which said measurement electrode served as said combustible catalyst.
3. The gas sensor according to claim 1, wherein said hydrocarbon prevention filter is made of a zeolite membrane.
4. A method of measuring a hydrocarbon concentration in a gas to be measured by utilizing the gas sensor set forth in claim 1, comprising the steps of: measuring an oxygen concentration in a gas to be measured, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said combustion catalyst, by said oxygen measurement means; calculating an oxygen concentration difference between said oxygen concentration measured in a gas to be measured, from which only combustible components are removed; and calculating a hydrocarbon concentration in a gas to be measured on the basis of the thus obtained oxygen concentration difference.
5. A gas sensor for measuring a hydrocarbon concentration in a gas to be measured, comprising: a first sensor portion including a hydrocarbon prevention filter for preventing a pass of hydrocarbons, a first combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter, and a first oxygen measurement means for measuring a first oxygen concentration in a gas to be measured from which said combustible components are removed by said first combustion catalyst; a second sensor portion including a second combustion catalyst for removing combustible components in a gas to be measured, and a second oxygen measurement means for measuring a second oxygen concentration in a gas to be measured from which said combustible components are removed by said second combustion catalyst; and a process means for calculating an oxygen concentration difference between said first oxygen concentration measured by said first oxygen measurement means and said second oxygen concentration measured by said second oxygen measurement means and then calculating a hydrocarbon concentration in a gas to be measured on the basis of the thus calculated oxygen concentration difference.
6. The gas sensor according to claim 5, wherein said first oxygen measurement means and said second oxygen measurement means comprises respectively: an oxygen ion conduction member; a measurement electrode arranged on one main plane of said oxygen ion conduction member, which is disposed to a gas to be measured; and a reference electrode arranged on the other main plane of said oxygen ion conduction member, which is disposed to a reference gas; in which said measurement electrode serves as said first combustion catalyst in said first oxygen measurement means and said second combustion catalyst in said second oxygen measurement means.
7. The gas sensor according to claim 5, wherein said hydrocarbon prevention filter is made of a zeolite membrane.
8. The gas sensor according to claim 6, wherein said oxygen ion conduction member of said first oxygen measurement means and said oxygen ion conduction member of said second oxygen measurement means are integrally formed.
9. A method of measuring a hydrocarbon concentration in a gas to be measured by utilizing the gas sensor set forth in claim 5, comprising the steps of: measuring a first oxygen concentration in a gas to be measured, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said first combustion catalyst, by said first oxygen measurement means; measuring a second oxygen concentration in a gas to be measured, from which combustible components are removed by said second combustion catalyst, by said second oxygen measurement means; calculating an oxygen concentration difference between said first oxygen concentration measured by said first oxygen measurement means and said second oxygen concentration measured by said second oxygen measurement means; and calculating a hydrocarbon concentration



in a gas to be measured on the basis of the thus calculated oxygen concentration difference.

- 5 10. A gas sensor for diagnosing a malfunction of an exhaust gas purifying apparatus in automobiles, comprising: a sensor including a hydrocarbon prevention filter for preventing a pass of hydrocarbons, a combustion catalyst for removing combustible components in a gas to be measured which is passed through said hydrocarbon prevention filter, and an oxygen measurement means for measuring an oxygen concentration of a gas to be measured from which said combustible components are removed by said combustion catalyst; and an indication means for indicating a malfunction of said exhaust gas purifying apparatus for a driver, when an oxygen concentration difference between said oxygen concentration in a gas measured by said oxygen measurement means and an oxygen concentration in a gas measured by an oxygen sensor for controlling an air/fuel ratio in an engine reaches to an oxygen concentration equivalent to a regulation level of hydrocarbons.
- 10 11. A method of diagnosing a malfunction of an exhaust gas purifying apparatus by utilizing the gas sensor set forth in claim 10, comprising the steps of: measuring an oxygen concentration in an exhaust gas passed through said exhaust gas purifying apparatus, from which hydrocarbons are removed by said hydrocarbon prevention filter and further combustible components are removed by said combustion catalyst, by said oxygen measurement means; calculating an oxygen concentration difference between said oxygen concentration measured by said oxygen measurement means and an oxygen concentration measured by said oxygen sensor for controlling an air/fuel ratio of an engine; and indicating a malfunction of said exhaust gas purifying apparatus for a driver when the thus calculated oxygen concentration difference reaches to an oxygen concentration equivalent to a regulation level of hydrocarbons.
- 15 20 25 30 35 40 45 50 55

**FIG. 1**

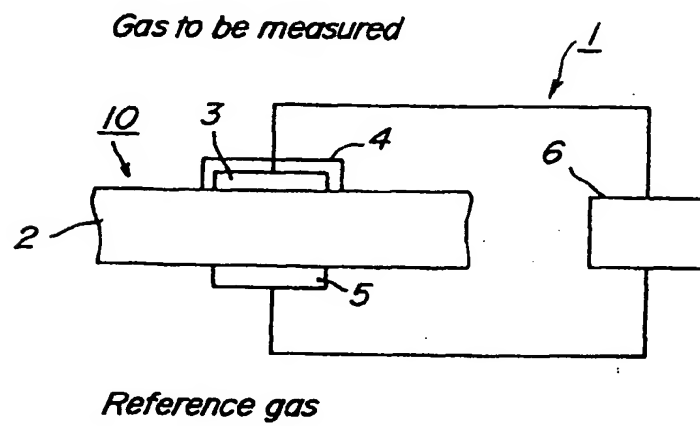
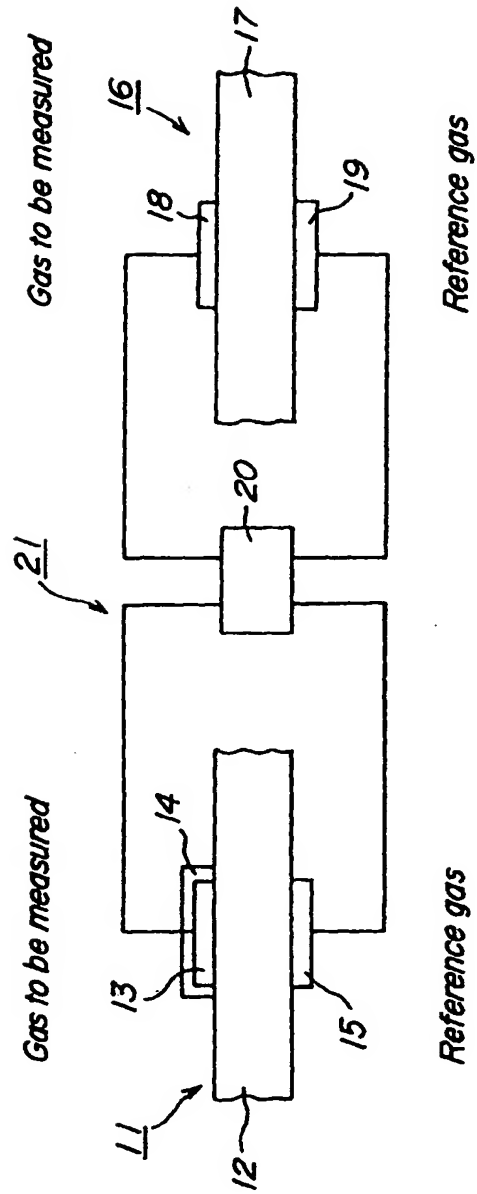


FIG. 2



**FIG. 3**

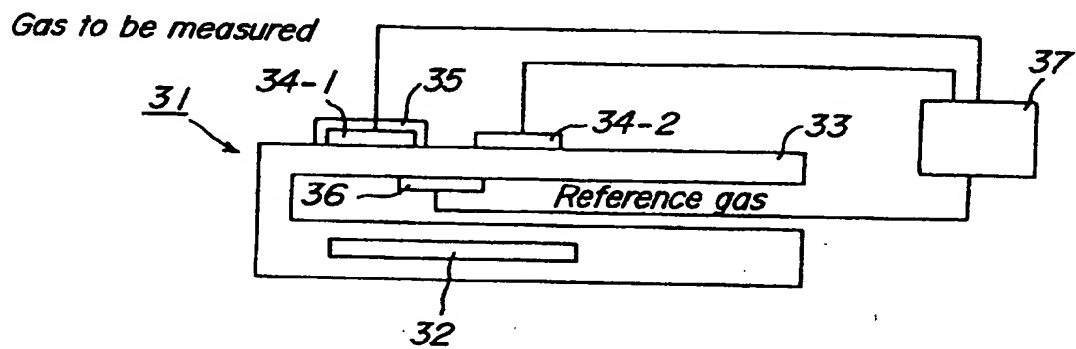
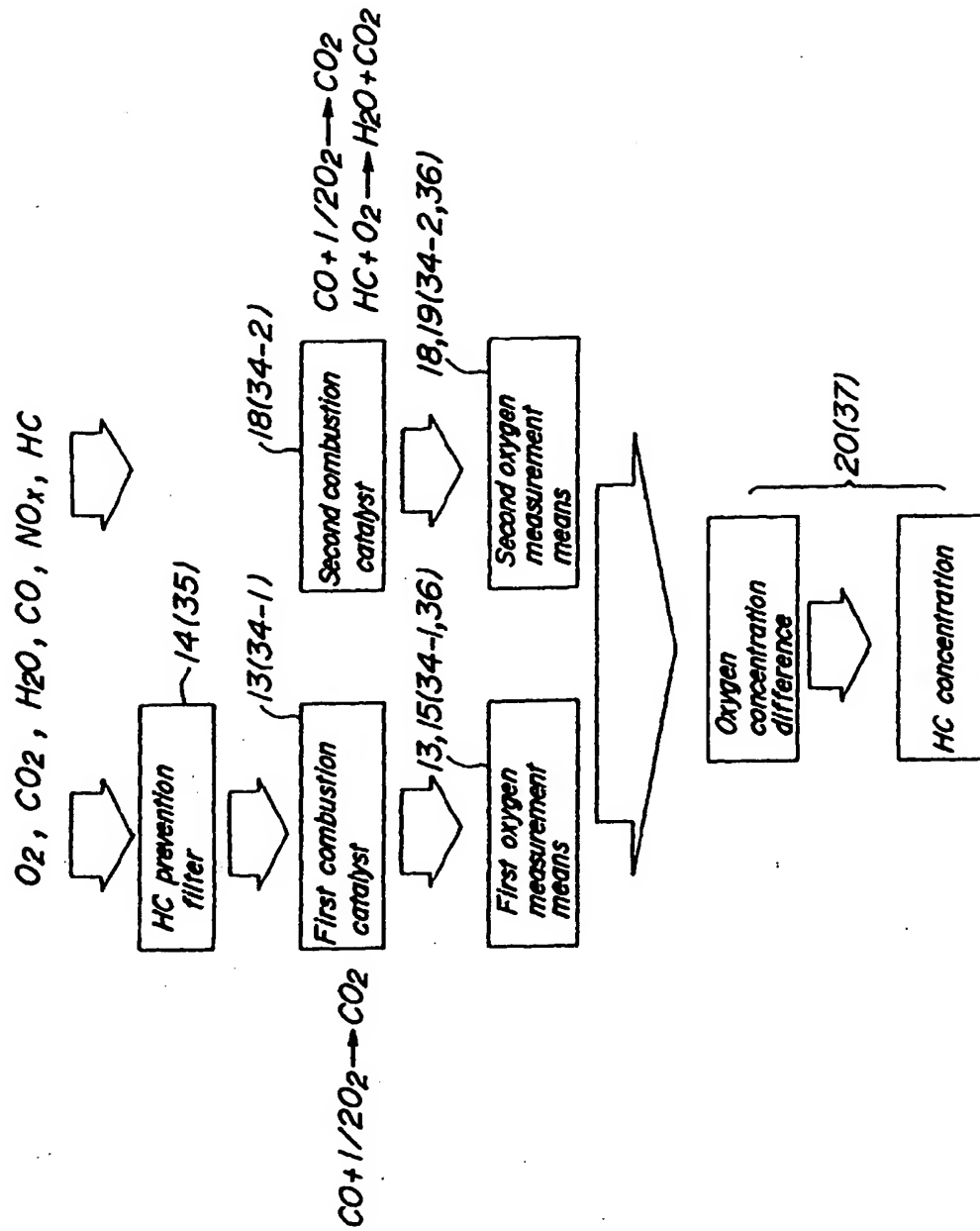
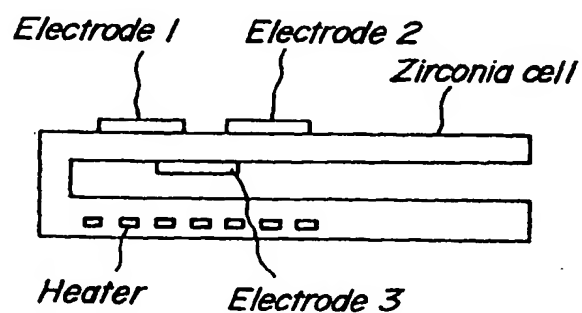


FIG. 4



**FIG. 5**



**FIG. 6**

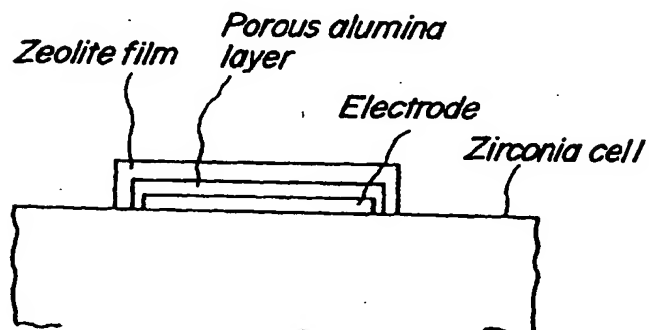
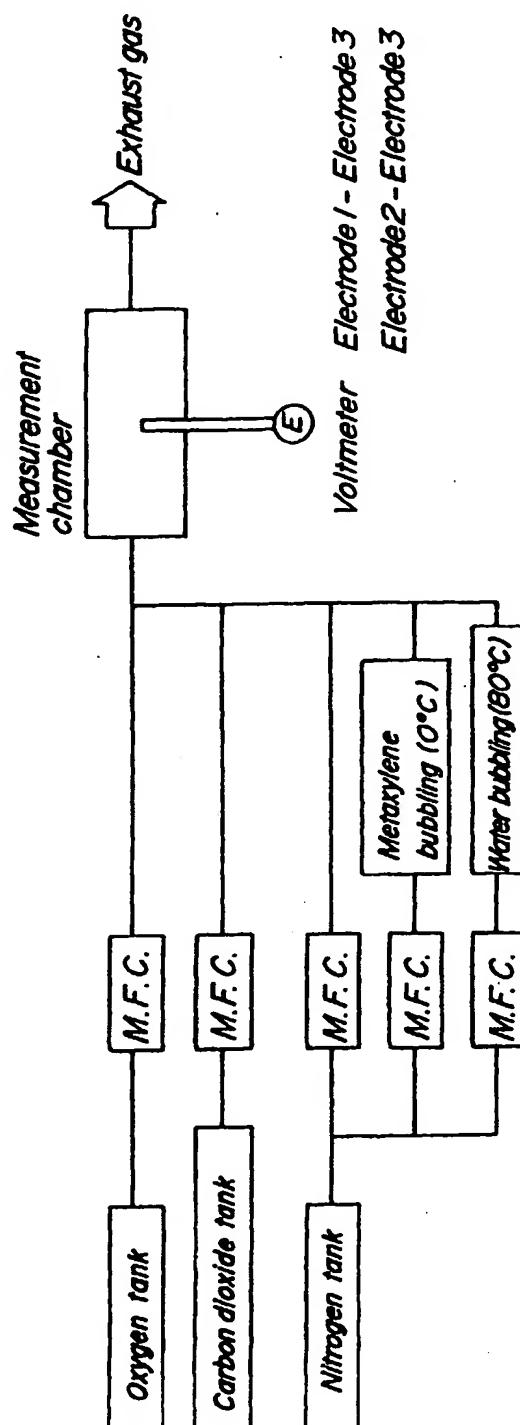
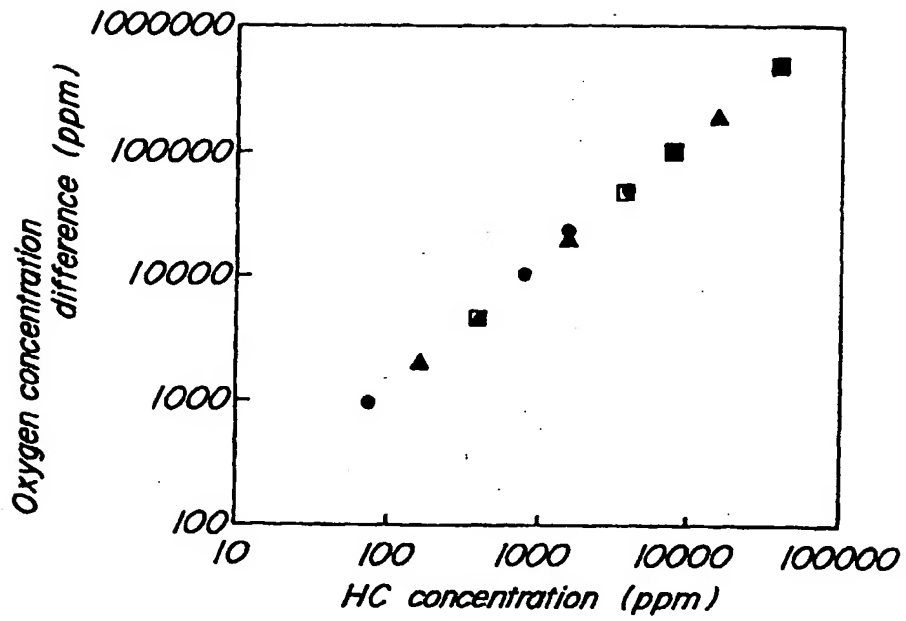


FIG. 7





**FIG. 8**



(19)



Europäisches Patentamt  
European Patent Office  
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(11)

EP 0 848 250 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
03.05.2000 Bulletin 2000/18

(51) Int Cl.7: G01N 27/407, F01N 7/00

(43) Date of publication A2:  
17.06.1998 Bulletin 1998/25

(21) Application number: 97309954.2

(22) Date of filing: 10.12.1997

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

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(30) Priority: 10.12.1996 JP 32961996

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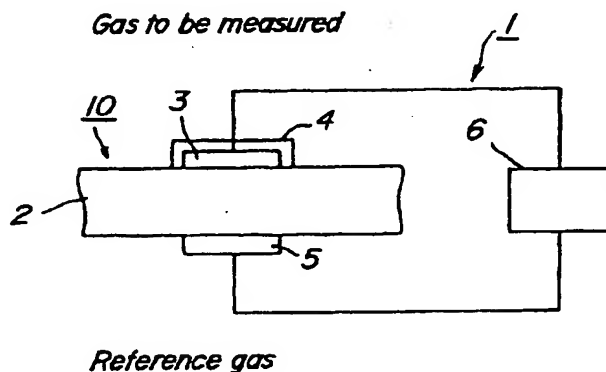
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(54) Gas sensor and method for diagnosing malfunction of exhaust gas purifying apparatus

(57) In a gas sensor for measuring a specific gas component especially hydrocarbon in a gas to be measured, a hydrocarbon prevention filter (4) preferably made of zeolite is used. There is obtained the oxygen concentration difference between (i) the oxygen concentration in the gas being measured from which hydrocarbons are removed by the hydrocarbon prevention fil-

ter and further combustible components are removed, measured by a cell (2,3,5), and (ii) a known oxygen concentration or an oxygen concentration in the gas from which only the combustible components are removed. The oxygen amount necessary for a combustion of hydrocarbons is then calculated to provide the hydrocarbon concentration in the gas to be measured.

FIG. 1



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 9954

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP 0 603 945 A (ENIRICERCH SPA ;SNAM SPA (IT)) 29 June 1994 (1994-06-29) * the whole document *	1-3	G01N27/407 F01N7/00
A	---	4,5,9	
Y	EP 0 743 431 A (NGK INSULATORS LTD) 20 November 1996 (1996-11-20) * the whole document *	1,2	
A	---	10,11	
Y	US 5 296 196 A (TAKESHIMA SHINICHI) 22 March 1994 (1994-03-22) * abstract * * column 2, line 26-34 *	3	
A	---	7	
A	US 5 313 791 A (HAMBURG DOUGLAS R ET AL) 24 May 1994 (1994-05-24) * column 1, line 13 - column 5, line 30; figure 2 *	10,11	
A	KOLTSAKIS G C ET AL: "DETECTION OF AUTOMOTIVE CATALYSTS FAILURE BY USE OF ON-BOARD DIAGNOSTICS" PROCEEDINGS OF THE INSTITUTION OF MECHANICAL ENGINEERS, XX, XX, vol. 209, no. D03, 1 January 1995 (1995-01-01), pages 171-182, XP000648261 * paragraph '04.1!; figure 3 *	10,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) F01N G01N
A	US 5 408 215 A (HAMBURG DOUGLAS R) 18 April 1995 (1995-04-18) * abstract *	10	
A	DE 44 08 504 A (BOSCH GMBH ROBERT) 21 September 1995 (1995-09-21) * abstract; figure 1 *	10	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 6 March 2000	Examiner Brison, O
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 30 9954

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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06-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0603945 A	29-06-1994	IT 1256759 B	15-12-1995
		AT 163092 T	15-02-1998
		DE 69316862 D	12-03-1998
		DE 69316862 T	03-09-1998
		ES 2113480 T	01-05-1998
		GR 3026284 T	30-06-1998
		JP 6229963 A	19-08-1994
		US 5400643 A	28-03-1995
EP 0743431 A	20-11-1996	JP 8285809 A	01-11-1996
		US 5772965 A	30-06-1998
US 5296196 A	22-03-1994	JP 2876793 B	31-03-1999
		JP 4248453 A	03-09-1992
US 5313791 A	24-05-1994	US 6005699 A	21-12-1999
		DE 69208401 D	28-03-1996
		DE 69208401 T	04-07-1996
		EP 0521641 A	07-01-1993
		JP 5196555 A	06-08-1993
US 5408215 A	18-04-1995	CA 2077152 A	05-03-1993
DE 4408504 A	21-09-1995	AU 1754295 A	03-10-1995
		CN 1124522 A	12-06-1996
		WO 9525277 A	21-09-1995
		EP 0698208 A	28-02-1996
		JP 8510840 T	12-11-1996

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office. No. 12/82

